Abstract

3-(Dimethylamino)-1-substituted prop-2-en-1-ones were transformed to pyiridines and pyridine-*N*-oxides *via* [2+2] cycloaddition, followed by cyclocondensation. We examined the reactivity of the ester groups and prepared the corresponding bicyclic systems. Reactions between electron-poor acetylenes and 3-(dimethylamino)-1-substituted but-2-en-1-ones have not yet been thoroughly studied, so we decided to prepare the enaminones *via* condensation between *N*,*N*-dimethylacetamide dimethyl acetal and methyl ketones or compounds with an active methylene group. We examined the reactivity of the system in [2+2] cycloadditions and concluded, that the presence of the methyl group hinders the reaction.

While preparing 3-(dimethylamino)-1-substituted but-2-en-1-ones, we also observed small amounts of benzene side products. We learned that these were formed when reactions took place in a microwave unit, at elevated temperatures, in solvent-free conditions and when 2.5 equivalents of *N*,*N*-dimethylacetamide dimethyl acetal were added. The reaction seems to progress as a double condensation between the starting compounds, being methyl ketones or active methylene compounds, and the amide acetal, followed by cyclocondensation to the corresponding benzene derivatives. We realised that we found a facile, convenient, one-pot synthesis of benzene derivatives, without the use of metal catalysts.

The method was extended to carboxamides, leading to pyridine derivatives. Pyridines were also synthesised from methyl ketones in a three step reaction. 3-(Dimethylamino)-1-substituted but-2-en-1-ones were prepared from methyl ketones using conventional heating. Substitution of the dimethylamino group with an amine group followed in the second step. In the last step the reaction with *N*,*N*-dimethylacetamide dimethyl acetal was followed by cyclocondensation to form the final pyridine products. The same reaction sequence was also applied to carboxamides in an attempted pyrimidine synthesis, but the dimethylamino group of acetamidines was not displaceable with an amino group under acidic conditions, instead the starting carboxamides were formed. We decided to test the displacement of the dimethylamino group with *C*-nucleophiles. Reactions with the *in situ* prepared 2-phenyl-oxazolone led to *N*-(1-(5-oxo-2-phenyloxazol-4(5*H*)-ylidene)ethyl)(hetero)aryl carboxamides in good yields. We examined their reactivity and transformed them further to conjugated enamine systems, using amide acetals. These systems reacted with maleic anhydride to form *N*,*N*-dimethyl-7-(substituted)-1,3-dioxo-1,3-dihydroisobenzofuran-4-carboxamides.

We also studied the [2+2] cycloaddition of electron-poor acetylens and »push-pull« butadienes, assesed factors that govern their reactivity, and prepared new products.

By using cheap and commercially available starting materials and reagents, we were able to prepare various carbocyclic and heterocyclic final products using relatively simple synthetic steps.

Keywords: facile synthesis, pyridines, benzene derivatives, amide acetals, enaminones